Chemical oxidation as repairing technique of damaged corrosion resistance enhanced anodic oxide film

Davide Prando[1], Davide Nicolis[2], Marco Ormellese[3,6], Fabio Bolzoni[4], MariaPia Pedeferri[5,6]

[1] Politecnico di Milano, Dipartimento di Chimica, Materiali e Ingegneria Chimica
"Giulio Natta", Milan, Italy, davide.prando@polimi.it
[2] Politecnico di Milano, Dipartimento di Chimica, Materiali e Ingegneria Chimica
"Giulio Natta", Milan, Italy, davide1.nicolis@mail.polimi.it
[3] Politecnico di Milano, Dipartimento di Chimica, Materiali e Ingegneria Chimica
"Giulio Natta", Milan, Italy, marco.ormellese@polimi.it
[4] Politecnico di Milano, Dipartimento di Chimica, Materiali e Ingegneria Chimica
"Giulio Natta", Milan, Italy, fabio.bolzoni@polimi.it
[5] Politecnico di Milano, Dipartimento di Chimica, Materiali e Ingegneria Chimica
"Giulio Natta", Milan, Italy, mariapia.pedeferri@polimi.it6
[6] Consorzio INSTM, UdR Politecnico di Milano, Firenze

Abstract

Titanium, as other light metals, shows enhanced corrosion resistance when properly anodized. This technique was already proved effective in several aggressive environments (mainly halides) in past works. However, it could be subject to failure in case of localized removal of oxide film due, for example, to incorrect handling during transport, installation, or use. Depending on part size and usage, a new anodizing treatment could be not feasible. In this case, localized chemical oxidation treatment could be used to recover damaged film and restore corrosion resistance. Chemical oxidation was performed on titanium by immersion in NaOH 10M and H_2O_2 10M at temperature from room to 90°C with duration ranging between 1h and 72h. Potentiodynamic tests in bromides 0.5M were used to determine the effectiveness of the treatment in relation with the one obtained with anodic oxidation. Higher bath temperature led to faster growth of the film, however it has no effect on the final corrosion resistance achievable. Samples pitting potential in bromides increased with treatment duration up to the establishment of a plateau that appears at lower time as temperature is increased. Titanium sample anodized and then scratched to simulate film mechanical removal was recovered using chemical oxidation and initial corrosion resistance was restored. The suggested treatments for in-situ recovery are 72h of exposure to NaOH or 6h at H_2O_2 at room temperature.

Keywords Titanium oxidation; chemical oxidation; anodizing; TiO_2; surface treatment

Introduction

Titanium and its alloys are widely appreciated for their high corrosion resistance in environments that are critical even for high-end stainless steel (duplex UNS S31803 and UNS S32750), such as concentrated chlorides [1, 2]. This resistance is due to a thin (1.5 nm - 10 nm) [3] but compact oxide layer that is naturally formed when the metal is exposed to the air. For this property, together with high strength, high fracture toughness and low density, [4, 5] titanium is used where other metals would fail, such as offshore, acid environment, aerospace [6, 7], automotive, high temperature, chemical & food industry [8–10], marine hydrometallurgical application and nuclear fuel wastes containment. [11–14]

In such aggressive environments, commercially pure titanium may suffer different form of corrosion. [15, 16] The most criticals of them are due localized breaking of passive layer and this is favored by the presence of concentrated halides, such hot salty water (above 200°C) or bromide containing species. [3, 17]

To further improve titanium corrosion resistance in these environments, specific treatments can be employed. It is the case of inclusion of elements that promote cathodic reaction, such as palladium [18], or nitration, that consist in introducing nitrogen in the first µm of the surface to promote the formation of TiN and increase corrosion resistance. [19, 20] These methods, acting on titanium composition, are effective but complicated to perform and expensive as well other surface coating techniques, such as vacuum plasma spray coating, plasma spraying and chemical vapor deposition.[21]

For this reason, treatments that act on the naturally formed passive layer are preferred. The easiest and cheapest treatment to tune oxide layer is anodic oxidation, that consists in applying an anodic polarization of several tens of volts to the metal, promoting the growth of the natural oxide layer with thicknesses from about 40 nm with anodizing potential 10 V, to about 250 nm at 100 V. [22, 23]

Anodic oxidation produces a compact, adherent and corrosion resistant oxide and was studied in previous works [24, 24, 25]. However, in case of already installed part, localized treatment, small part or complex geometry, anodic oxidation could be un-feasible. In these cases chemical oxidation, not requiring any applied current and particular cell setup, would be suitable to provide the corrosion resistance enhancement needed. Moreover, chemical oxidation can be used to restore mechanically disrupted oxide continuity. Abrasions and scratches during parts transport or installation can lead to lack of protection where anodic oxide is locally removed. In-situ recovery prevents the need of part re-treatment.

Most common reagents used for chemical oxidation are alkoxides (e.g. NaOH, KOH) and hydrogen peroxide [26–28]. Sodium and potassium hydroxide dissociate in water releasing metal cation and hydroxide anion. Contrary of the amphoteric metals (Al, Zn, Sn, Pb), which in alkaline environment forms soluble metal hydroxide, titanium is favored by hydroxide, that promotes the formation of its passivity oxide. [29] Hydrogen peroxide treatment has been less investigated in literature compared to alkoxides, the proposed mechanism of oxide formation pass through numerous intermediates [27]

$$M^{n+} + H_2O_2 \rightarrow M^{(n+1)+} + OH \bullet + OH^-$$

$$M^{n+} + OH \bullet \rightarrow M^{(n+1)+} + OH^-$$

$$OH \bullet + H_2O_2 \rightarrow H_2O + HO_2$$

$$M^{n+} + HO_2 \rightarrow M^{(n+1)+} + HO_2^-$$

$$HO_2 \rightarrow H^+ + O_2^-$$

$$M^{(n+1)+} + O_2^- \rightarrow M^{n+} + O_2$$

Which leads to the competing reactions of formation of titanium dioxide and evolution of oxygen: [30]

$$Ti + 2H_2O_2 \rightarrow TiO_2 + 2H_2O$$

$$2H_2O_2 \rightarrow H_2O + O_2 \uparrow$$

The purpose of this work was to find key parameters that influence chemically promoted oxide layer, and to tune them in order to achieve the highest corrosion resistance and to use this treatment to spot recover oxide on previously anodized parts.

Materials and Methods

Square samples 20x20x1.6 mm were cold-cut from a titanium UNS R50400 (ASTM grade 2) sheet, polished with 100 and 300 grit SiC paper and degreased with EtOH in ultrasonic bath for 4 minute. Then rinsed in distilled water with the same ultrasound exposure.

Alkoxides

NaOH was used as representative of the alkoxide family for its ease of production and storage, and for its tendency to produce less porous and more compact oxide film. [26] Treatments were performed by submerging titanium samples in 100 ml beakers. Values of investigated parameters are:

- Duration: 3h - 6h - 12h - 24h - 72h
- Treatment temperature: 25°C - 60°C
- Quantity of solution: 10 ml - 50 ml - 100 ml
- Solution concentration: 10 M - 50 M

Temperature was maintained below 60°C to avoid excessive hydrogen embrittlement due to the formation of titanium hydrides with hydrogen generated by the secondary reaction:[29]

$$Ti + 2H_2O \xrightarrow{\mathrm{OH^-}} TiO_2 + 2H_2 \uparrow$$

Post-treatment annealing was performed on some samples to convert sodium titanate hydrogel, formed on the surface during chemical oxidation, into amorphous titanate layer, to reduce protective layer porosity. [31, 32] Temperature was maintained to either 400°C, 500°C or 600°C for 1h in air.

Hydrogen Peroxide

Hydrogen peroxide treatments were performed in H_2O_2 solution 10 M, prepared just before the treatment from a master solution 35% wt. stored at 5°C to prevent thermal decomposition. Treatments were performed in 50 ml or 100 ml of solution, with duration ranging from 6h to 24h and temperatures from 25°C to 90°C. Due to the high decomposition rate of H_2O_2, solution quantities below 50 ml were not tested, to prevent excessive decrease in solution concentration during test.

Annealing was performed at either 350°C, 400°C, 450°C, 500°C, 600°C or 700°C for 1h, as they are reported to be able to positively modify surface morphology by decomposing oxygen bubbles from the gel layer of the reaction products attached to the surface, causing the appearance of grooved structure on the surface during the heating process.[28]

Microscopy

After chemical oxidation, field emission SEM FEI Nova nanoSEM 450, and tungsten filament SEM Stereoscan 360 were used to characterize samples morphology and oxide thickness. Sacrificial samples were bent to a narrow curvature radius to promote film descaling. Scales detached in this way were gold sputtered and observed in cross-section.

The presence of crystalline structure in the oxides was detected using XRD technique with a diffractometer model Phillips PW 1830, able to generate a Cu-Kα radiation with a wavelength of 0.154 nm. This technique does not allow the measurement of absolute crystalline fraction, but was used to detect the presence of sodium titanate after NaOH treatments of different durations, comparing the amount by normalizing sodium titanate peaks height with the titanium principal one.

Corrosion resistance

Samples corrosion resistance were characterized with potentiodynamic tests performed with MetroOhm Autolab potentiostat M204. A standard 1 liter, 3-electrode cell was used, including an activated titanium counter electrode, a silver/silver chloride (SSC) counter electrode and the working electrode with 1 cm^2 of exposed area. Open circuit potential (OCP) was recorded after 1h of sample exposure to the testing solution. Then potential was scanned from 100 mV below the OCP up to 8 V SSC with a scan rate of 20 mV/min. Anodic current and potential difference between metal and reference electrode were registered with Nova® 2.1.1 software.

To assess titanium resistance to corrosion it is necessary to distinguish different forms of corrosion. By recognizing that for titanium the most dangerous and difficult to identify is localized corrosion, the effectiveness of different halides in promoting localized oxide breakdown was studied [33]. As result, the corrosion test were performed in 0.5 M ammonium bromide solution, that was proven to be the most effective in promoting localized corrosion. A current density of 10 A/m^2 was chosen as threshold to define localized oxide breakdown events.

As the duration of each test did not exceed 8h, no sealing was necessary. Previous works on titanium oxide tested in such conditions showed that nor chemical ($\Delta pH \approx 0.05$) nor physical ($\Delta T \approx 2°C$) deviations were to be expected. [25] In order to ensure repeatability, a minimum of three measurements were made for each treatment procedure.

Scratch

To simulate an abrasion event occurred during part transportation, installation or usage, anodized samples were scratched, leading to a partial removal of protective oxide. Scratched samples were then vibrated in EtOH and rinsed in water to remove possible SiC embedded particles.

For a reproducible scratching procedure, a rectangular strip of grit 300 SiC paper (1 cm x 4 cm) was dragged over the titanium coupon for its whole length, being subjected to a weight of 1 kg over its 4 cm^2 surface. Supports of the same height and material as the samples were placed before and after the sample's length, to assure a uniform applied pressure during scratching (Fig. 1).

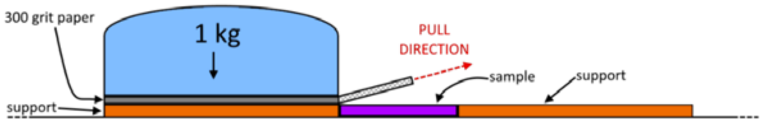

Figure 1 Scheme of scratching mechanism.

Anodized and scratched samples were then subject to chemical oxidation to repair removed oxide and recover original anodized samples corrosion resistance.

Results and Discussion

Solution concentration and quantity

The effect of the volume of solution used to treat samples in NaOH on titanium corrosion resistance is shown in Fig. 2.

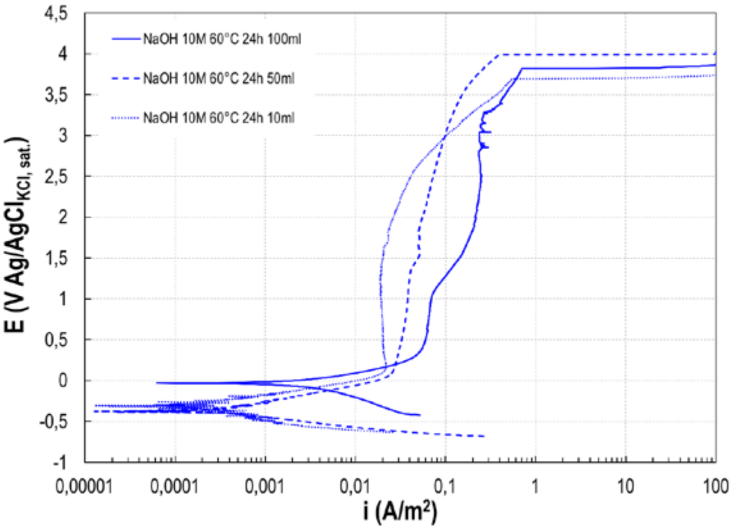

Figure 2 Effect of NaOH treatment solution volume on samples corrosion resistance to bromides 0.5M

The three plotted curves are good representation of all the repeatability performed, they show that passing from 10 ml to 100 ml, keeping constant the sample dimension (20x20x1.6 mm), the effect on localized corrosion is within the experimental error. The same phenomenon is observed with H_2O_2 treatment (Fig. 3) passing from 50 ml to 100 ml.

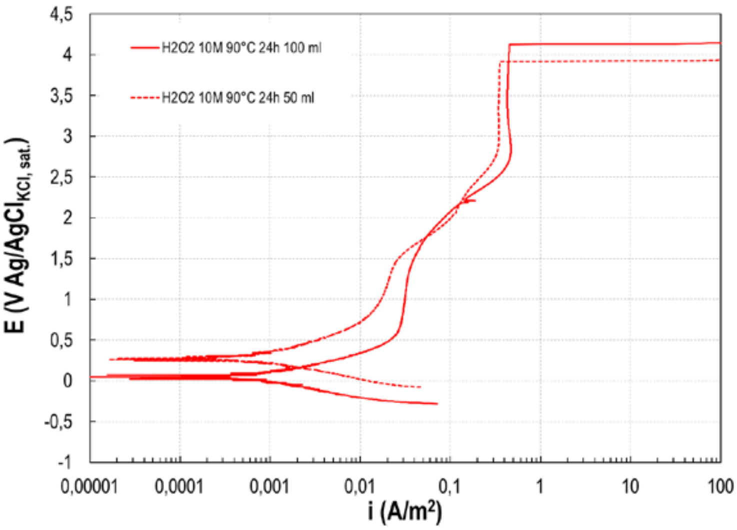

Figure 3 Effect of H_2O_2 treatment solution volume on samples corrosion resistance to bromides 0.5M

From this observation, two contrasting hypothesis were made:

- The chemically developed oxide growth has linear kinetic and the amount of reagent consumed in 24h at 60°C is lower than the one contained in 10 ml of solution 10 M. So it is not entirely consumed by the oxidation and an increased amount of available reagent does not contribute to oxide growth.
- The growth kinetic decreases exponentially so the film formed in the first stage leads to the shown increase in corrosion resistance, any further exposure to the solute contributes marginally to the oxide growth and the effect are not visible on the pitting potential.

To discern the correct hypothesis, the treatment was repeated with five time the initial concentration of NaOH (50 M). In case of linear growth the exposure to a more concentrated reagent would lead to an appreciably thicker oxide. On the other side, if after the initial oxidation the oxide growth velocity progressively slow down to negligible values, the higher concentration would not lead to higher corrosion resistance.

In Fig. 4 the effect of NaOH concentration increase from 10 M to 50 M is shown.

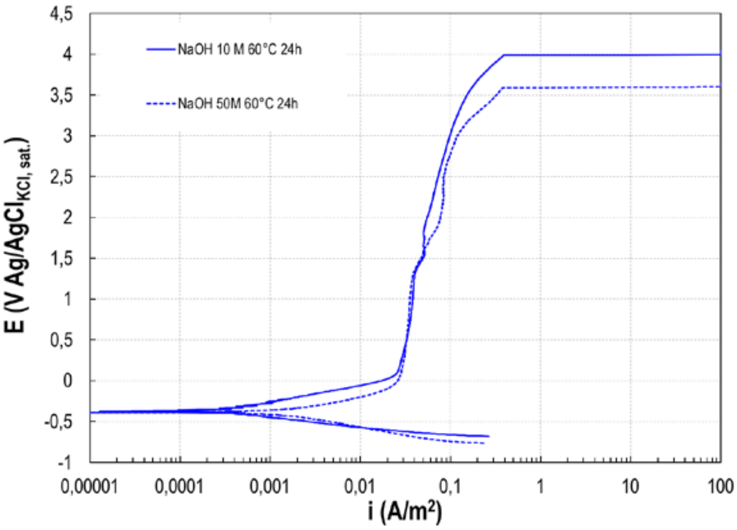

Figure 4 Effect of NaOH concentration on samples corrosion resistance to bromides 0.5 M

As no difference in corrosion resistance are observed with NaOH concentration increase, the existence of a plateau after which the treatment has no more effect is proven.

It is important to notice that, even if it does not affect final corrosion resistance, the increase in concentration modifies oxide growth kinetic enough to produce different aesthetic appearance of the oxide. Titanium oxide interference color is strongly dependent on oxide thickness, its variation (visible in Fig. 5) indicates a difference in oxide thickness on samples produced with 10 M and 50 M NaOH.

Figure 5 Sample aesthetic appearance changing passing from 10 M NaOH (left) to 50 M NaOH (right) treatment conducted for 24h at 60°C

Treatment duration and temperature

Under the hypothesis, confirmed by Fig. 4, that a plateau exist after which the oxide growth become too slow to affect corrosion resistance, the time of establishment of this plateau at a temperature of 60°C was searched. Fig. 6 shows the results of at least three potentiodynamic test performed on samples treated for 1h, 6h, 12h, 18h, 24h and 72h at 60°C in NaOH.

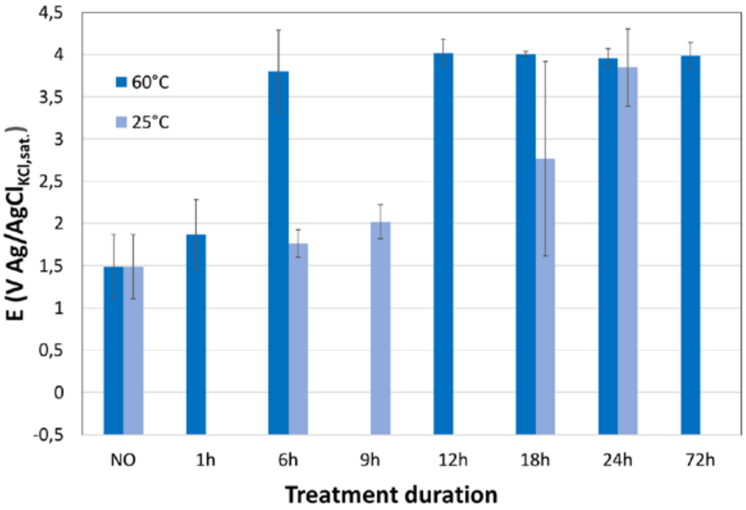

Figure 6 Effect of treatment temperature and duration on NaOH chemical oxidized samples corrosion resistance

After 12h of treatment, the increase of corrosion resistance become negligible and the only effect is a narrowing of results distribution.

The existence of a similar plateau was researched at room temperature, to simplify a possible in-situ treatment, without the requirement of local heat at 60°C for several hours. The results are shown in Fig. 6. Lowering the temperature has the effect to delay the reaching of the maximum corrosion resistance plateau. Note its final value is not influenced by treatment temperature.

To validate oxide growth kinetic hypothesis, SEM observations of oxide cross-section were performed. Results are shown in Fig. 7.

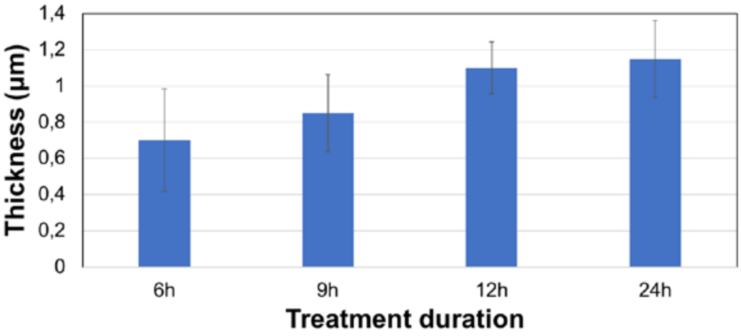

Figure 7 Effect of NaOH treatment duration on titanium oxide thickness

Oxide growth rate is about 117 nm/h in the first 6h, then 50 nm/h passing from 6h to 9h and 83 nm/h from 9h to 12h, but drop down to 4 nm/h from 12h to 24h of treatment. These data correlate the stabilization of corrosion resistance given by increasing treatment duration with oxide growth kinetic.

The same trend was found on H_2O_2 treatments, as reported in Fig. 8

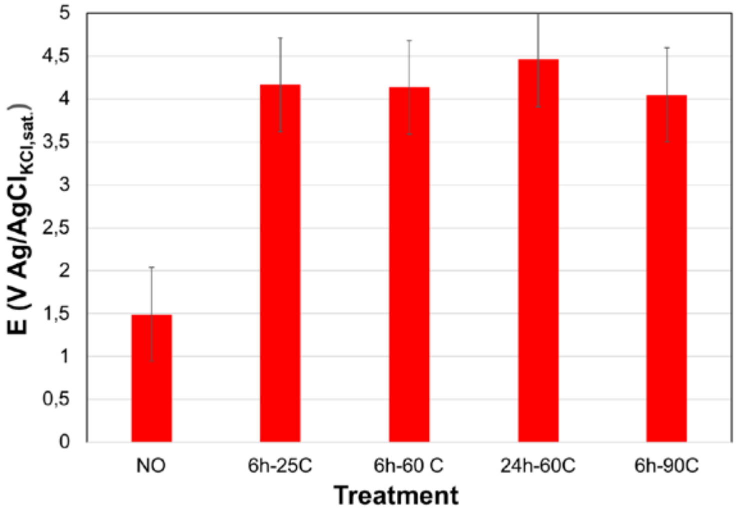

Figure 8 Effect of treatment temperature and duration on H_2O_2 chemical oxidized samples corrosion resistance

Increasing temperature from 25°C to 90°C and duration from 6h to 24h does not lead to any significant variation in corrosion resistance. The establishment of the plateau on H_2O_2 happens before 6h at 25°C, suggesting a faster kinetic compared to NaOH oxidation.

Post treatment annealing

To achieve better corrosion resistance in bromides, passing the 4 V pitting potential plateau observed in both NaOH and H_2O_2 treatments, annealing for 1h at 400°C and 600°C was performed. Results and comparison between the effect of calcination on samples chemically oxidized in both the solution and sample of non-treated titanium are shown in Fig. 9.

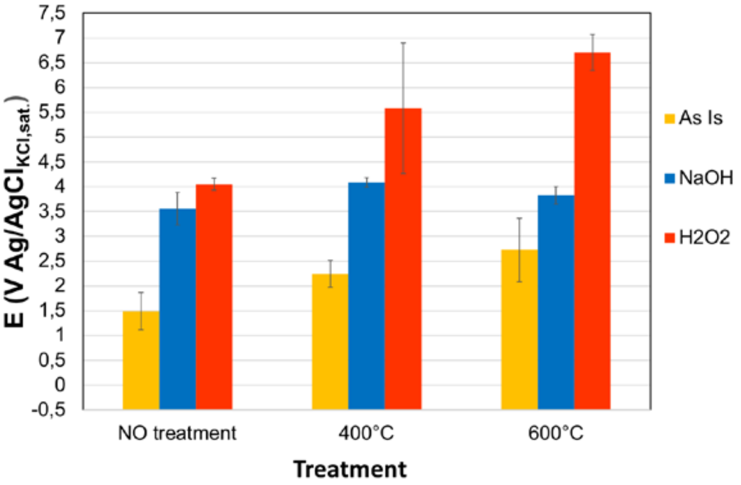

Figure 9 Effect of thermal treatments at 400°C and 600°C for 1h on non-treated titanium, NaOH oxidized titanium and H_2O_2 oxidized titanium

Thermal treatment has a moderate effect on corrosion resistance of non pre-oxidized titanium. This is due to the thickening of titanium dioxide layer due to thermal oxidation.

Annealing shows no effect at both temperatures on samples treated in NaOH. As a positive effect is reported in literature,[34] the reason of stationary corrosion resistance was searched on thermal treatment duration. Fig. 10 shows the effect of doubling the annealing duration.

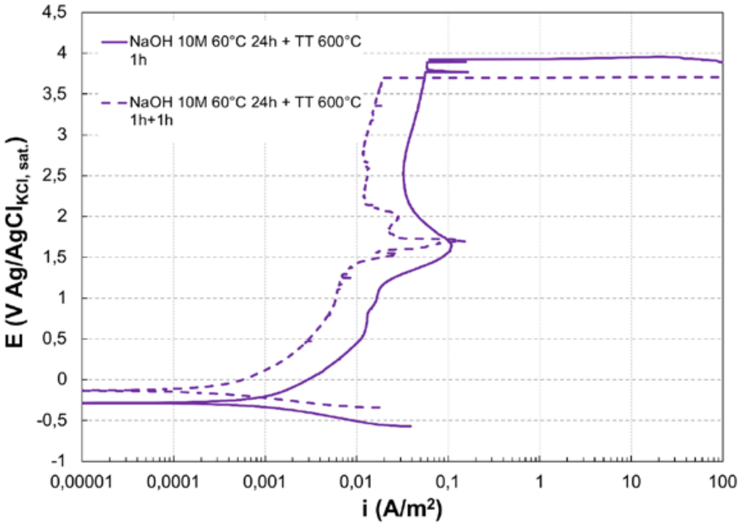

Figure 10 Effect of thermal treatments duration on corrosion resistance of samples oxidized in NaOH at 60°C for 24h

As no effect is observed by doubling calcination time the effective presence of sodium titanate gel available to be transformed was checked with XRD analyses. Fig. 11 shows the relative intensity of XRD peak associated with sodium titanate on the main titanium peak.

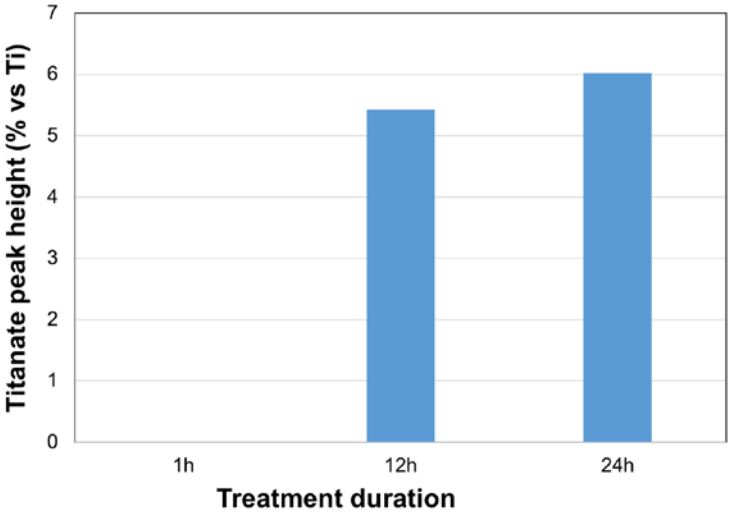

Figure 11 XRD analyses on samples treated in NaOH for 1h, 9h and 12h at 60°C

After 1h of treatment in NaOH at 60°C, titanate formation is too low to be revealed by XRD analyses, after 12h a small peak became visible. The minor peak increase between 12h and 24h shows the very slow kinetic of sodium titanate formation. Such a small quantity, although detectable, is not enough to produce a visible increase in corrosion resistance after thermal treatment.

Fig. 9 shows a remarkable effect of annealing on corrosion resistance of samples oxidized with H_2O_2, that exceeds 6.5 V of pitting potential after 600°C treatment. A positive effect is also observable on anodic current density at 1 V and 2 V of each curve, as shown in Fig. 12.

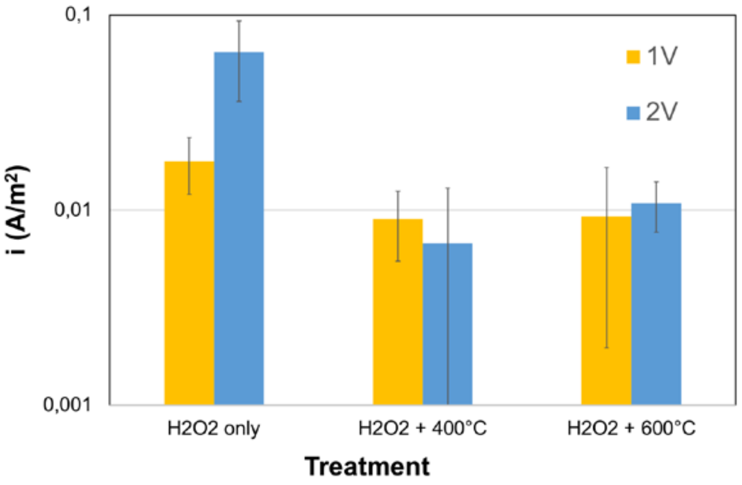

Figure 12 Effect on anodic current density at 1V and 2V of thermal treatments performed at 400°C and 600°C on H_2O_2 oxidized titanium

H_2O_2 treatment performed for 6h at 25°C forms oxide with disordered lamellar structure at the µm scale (Fig. 13). This structure is maintained with annealing up to 550°C while is recovered when calcination is performed above 600°C as shown in Fig. 14 This behavior is responsible to the enhanced corrosion resistance of samples treated at higher temperatures.

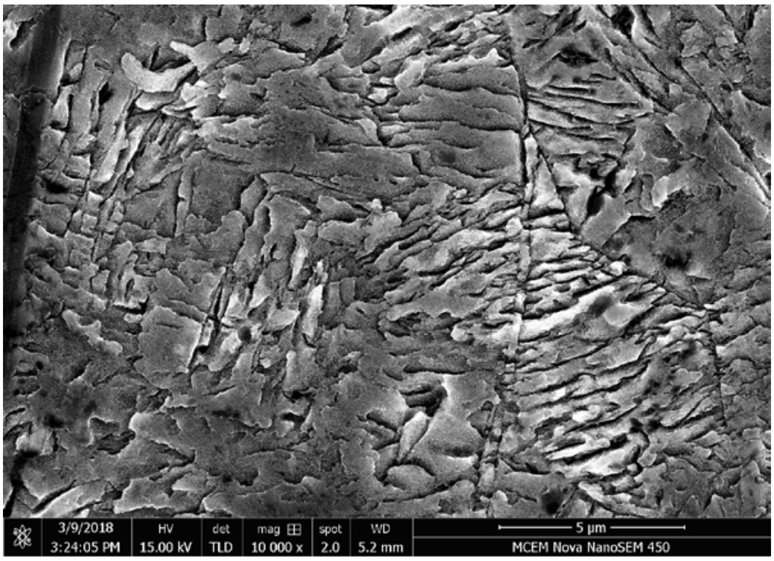

Figure 13 Surface morphology of samples treated in H_2O_2 for 6h at 25°C without any further treatment

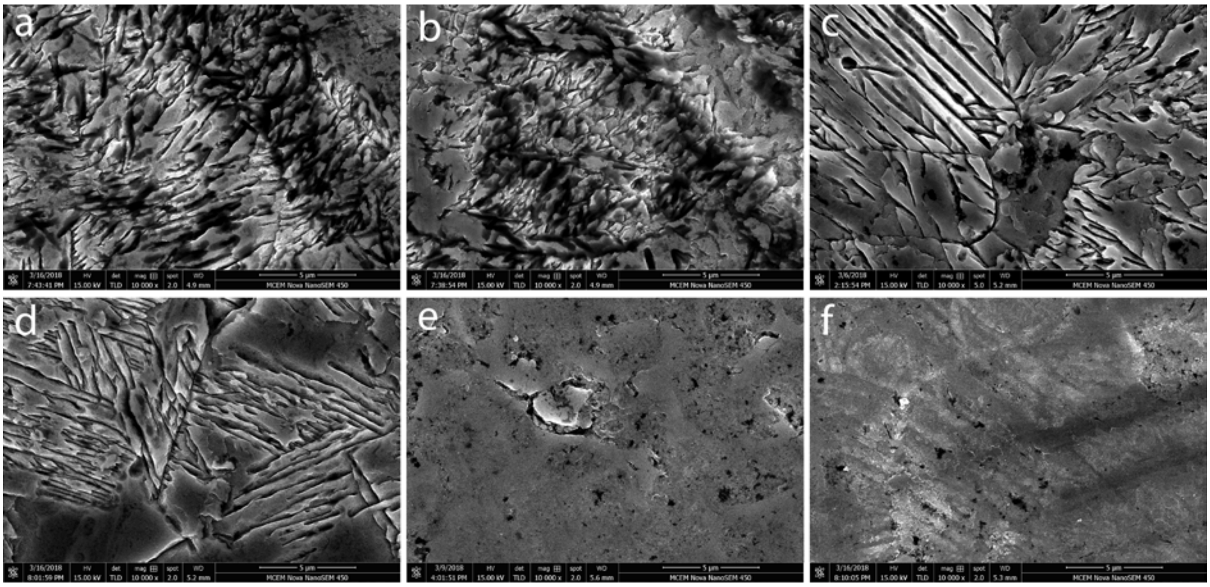

Figure 14 Surface morphology of samples treated in H_2O_2 for 6h at 25°C and subject annealing at: a) 350°C, b) 400°C, c) 450°C, d) 500°C, e) 600°C, f) 700°C

Recovery

The best representative of each treatment class tried so far was used to recover oxide layer on anodized samples subject to mechanical abrasion. To simulate an industrial anodizing process and keep power demand low, titanium samples were anodized at 20 V. Then, samples were scratched accordingly to previously described procedure and chemically oxidized in NaOH or H_2O_2.

In Fig. 15 pitting potentials in NH_4Br 0.5M of non treated sample, anodized sample, anodized and scratched sample and anodized, scratched and recovered are shown.

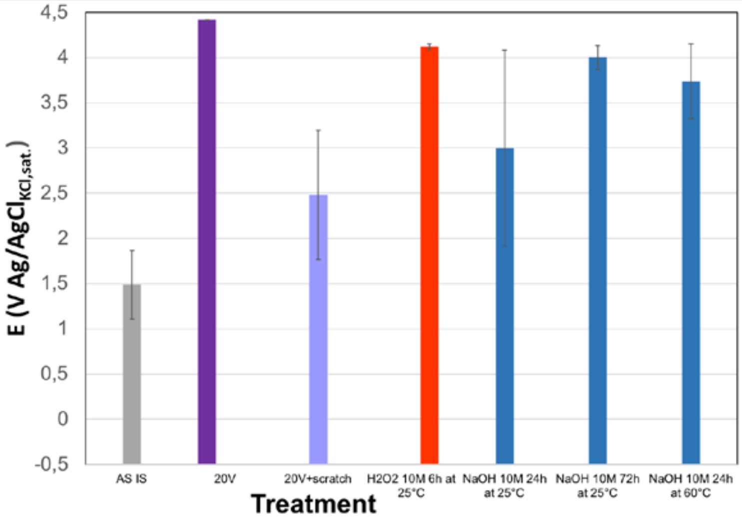

Figure 15 Comparison of pitting potential in NH_4Br 0.5M of samples subject to anodization or/and chemical oxidation treatment

Anodization process increases pitting potential of about 3 V even using a moderate potential. After scratch is performed, corrosion resistance abruptly decrease to values close to non treated one, with a high measure variability.

Although NaOH 10M treatment was theoretically able to increase pitting potential to 4 V in 24h at 25°C, to repair scratched treatments required 72h at 25°C or 24h by increasing the temperature at 60°C. Treatment at 25°C was more reliable and it is preferable not requiring in-situ solution heating.

H_2O_2 10M treatment was able to recover corrosion resistance in 6h at 25°C. This solution, although faster, it is more difficult to handle and more prone to self-decomposition.

Conclusion

Commercially pure titanium ASTM grade 2 was chemically oxidized using NaOH and H_2O_2. The effects of solution concentration, quantity and on corrosion resistance to NH_4Br 0.5 M environment were studied, together with the influence of treatment temperature, duration and the presence of post-treatment annealing.

A plateau of corrosion resistance was identified in both the oxidizing solution. After the establishment of that plateau, any further increase of treatment duration, temperature, solution concentration and solution quantity leads to a marginal increase of oxide thickness, without any noticeable effect on corrosion resistance. SEM oxide thickness measurement were performed to confirm the relation between corrosion resistance plateau and oxide thickness growth kinetic.

The maximum of corrosion resistance in NaOH is achieved after 12h at 60°C and after 24h at room temperature. H_2O_2 kinetic is faster and the same resistance is achieved before 6h at room temperature.

The effect of annealing at 400°C and 600°C was studied on samples treated in both the solutions. The independency of corrosion resistance of NaOH treated samples to calcination temperature was justified by the small amount of sodium titanate gel developed after 24h at 60°C reveled with XRD analyses.

Annealing was found to have a strong effect on pitting potential in bromides environment when applied to samples oxidized in H_2O_2. This is caused by the deep morphology changes happening at samples surface during thermal treatment.

Both NaOH and H_2O_2 10 M treatments were applied to anodized and then scratched samples to study possibility of in-situ treatment recovery. NaOH requires 24h at 60°C or 72h at 25°C to achieve the original corrosion resistance of 20 V anodized samples, while H_2O_2 only requires 6h at 25°C.

Further developments

Further works will be oriented in the determination of the minimum conditions to achieve corrosion resistance plateau, in form of minimum solution concentration and minimum treatment duration at room temperature.

Moreover, longer oxidations in NaOH will be performed to allow the development of enough sodium titanate to cause a visible increase of corrosion resistance after annealing.

Acknowledgment

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